

# PATENT SPECIFICATION

(11) 1286885

1286885  
1286885  
1286885

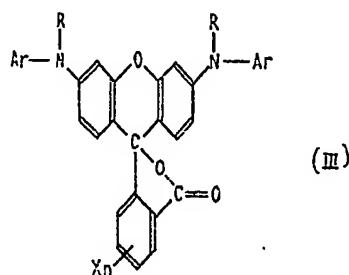
## NO DRAWINGS

- (21) Application No. 47924/70 (22) Filed 8 Oct. 1970  
 (31) Conventional Application No. 80540 (32) Filed 8 Oct. 1969 in  
 (33) Japan (JA)  
 (45) Complete Specification published 23 Aug. 1972  
 (51) International Classification C09B 57/00  
 (52) Index at acceptance C4P D1S

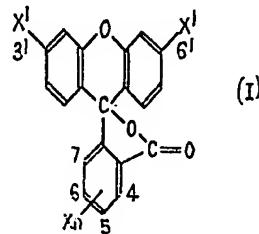


## (54) PROCESS FOR PREPARING FLUORANE COMPOUNDS

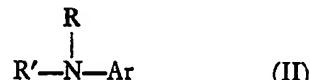
- (71) We, FUJI PHOTO FILM CO., LTD.,  
 a Japanese Company, of No. 210, Nakanuma,  
 Minami Ashigara-Machi, Ashigara-Kamigun,  
 Kanagawa, Japan, do hereby declare the  
 5 invention for which we pray that a patent  
 may be granted to us, and the method by  
 which it is to be performed, to be particu-  
 larly described in and by the following state-  
 ment:—
- 10 The present invention relates to a process  
 for preparing fluorane compounds.
- According to the invention, there is pro-  
 vided a process for preparing a fluorane com-  
 pound represented by the general formula  
 15 (III):



- wherein X represents a halogen atom, n is  
 20 an integer from 1 to 4, R represents an alkyl  
 group having from 1 to 5 carbon atoms and  
 Ar represents an aryl group, which comprises  
 condensing a fluorane derivative represented  
 by the general formula (I):



- 25 wherein X' represents a halogen atom and X  
 and n are as defined above with an arylamine  
 derivative represented by the general formula  
 (II):



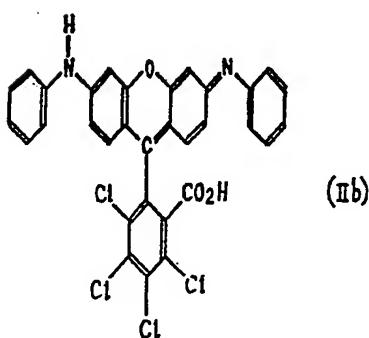
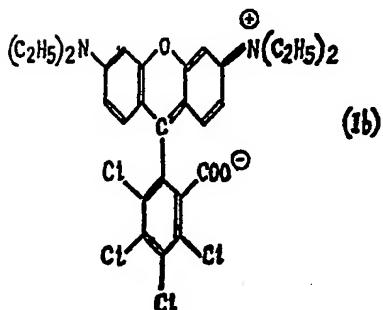
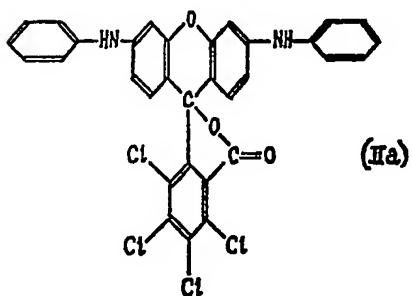
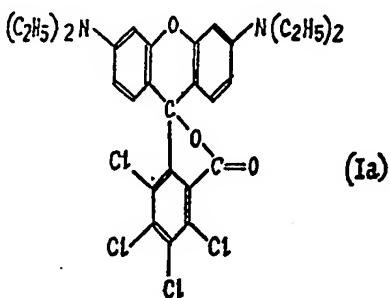
wherein R and Ar are as defined above and  
 R' represents a hydrogen atom or a methyl, 30  
 ethyl, benzyl, allyl or acetyl group.

The fluorane compounds represented by the  
 general formula (III) as claimed in our co-  
 pending U.K. application No. 47923/70  
 (Serial No. 1273454), wherein an alternative  
 process for preparing them is also claimed.  
 These compounds are substantially colourless  
 in themselves but when contacted with solid  
 acids such as bentonite, zeolite, acid clay or  
 trimagnesium silicate, organic acids such as  
 benzoic acid, benzenesulphonic acid or phenol,  
 or mineral acids such as hydrochloric acid,  
 sulphuric acid or perchloric acid, that is, so-  
 called electron acceptor materials, the fluorane  
 compound is immediately converted into a  
 dye having a colour varying from purple to  
 blue according to the particular fluorane com-  
 pound.

The fluorane compounds represented by  
 the general formula (III) are very stable on  
 exposure to the atmosphere or light and their  
 colour-forming ability is not affected by such  
 exposure. Also, the dye formed on contact  
 with an electron-acceptor material is very  
 fast to light. The fluorane compounds repre-  
 sented by the general formula (III), there-  
 fore, are very effective as precursors or colour-  
 formers for pressure-sensitive, heat-sensitive  
 and photo-sensitive copying papers (these are  
 developed by contact with an electron  
 acceptor material under pressure, heat or  
 light).

Several compounds similar to those repre-  
 sented by the general formula (III) are known  
 (see Beilstein, Handbuch Der Organische  
 Chemie, Vol. 19, 349). Examples of these  
 known compounds are represented by the  
 following formulae Ia and IIa but these com-  
 pounds cannot be obtained as colourless  
 crystals. It is believed that they exist rather  
 in the forms represented by the following  
 formulae Ib and IIb, which are dyes:

**SEE ERRATA SLIP ATTACHED**



- 5 The inventors have found that replacement of the dialkylamino and monoarylamino groups with N-alkyl-N-arylamino groups renders the lactone ring stable, so that the desired compound is obtained as a colourless material.
- 10 The compounds represented by the general formula (I) may be selected from hitherto

known compounds such as 3',4',4,5,6,7 - hexachlorofluorane and 3',6',4,7 - tetrachlorofluorane.

15 3',6' - Dichloro - 4,5,6,7 - tetrabromo - fluorane and 3',6' - dibromo - 5 - iodo - fluorane can be obtained by chlorinating or brominating the hydroxy groups of the corresponding fluorescein (3',6' - dihydroxy - fluorane) with phosphorus pentachloride or phosphorus pentabromide.

20 The compounds of the general formula (II) include N-methylaniline, N,N-dimethylaniline, N-allyl-N-methylaniline, N-methyl acetanilide, N-ethylaniline, N,N-diethylaniline, N-benzyl-N-ethylaniline, N-methyl-o-toluidine, N-methyl-p-anisidine, N-methyl-p-chloroaniline, N,N-dimethyl-p-chloroaniline, N-methyl-m-chloroaniline and N-methyl-β-naphthylamine.

25 The condensation reaction between the fluorane derivative represented by the general formula (I) and the arylamine derivative represented by the general formula (II) can be carried out by heating these compounds in the presence of zinc chloride and/or p-toluenesulphonic acid. The reaction may be conducted at 60-230°C, preferably 170-200°C, for from 1 to 6 hours.

30 The fluorane derivatives prepared by the process of the invention may be employed as precursor pigments in pressure, heat or light-sensitive copying papers.

35 The process of the invention is highly suitable for industrial use.

40 The following examples illustrate the present invention.

#### EXAMPLE 1

45 Preparation of 3',6'-bis(N-methyl-N-phenylamino)-4,5,6,7-tetrachlorofluorane.

50 A mixture of 10.2 g. (0.02 mole) of 3',6',4,5,6,7-hexachlorofluorane, 6.4 g. (0.06 mole) of N-methylaniline and 10 g. of zinc chloride was heated for 2 hours at 180-185°C., for 2 hours at 190-195°C. and for 2 hours at 210-220°C. The dye formed in the reaction was then dissolved in methanol, and poured into a large quantity of water. The precipitated dye was filtered off under suction, and washed with a small quantity of dilute hydrochloric acid.

55 On violently stirring the dye in a suspension of 300 ml. of 3% aqueous caustic soda solution and 300 ml. of toluene, the product formed by neutralization of said dye dissolved in the toluene.

60 The toluene layer was separated, washed several times with warm water and concentrated by evaporation under reduced pressure. The syrup-like matter obtained was mixed with a small quantity of acetone and cooled to obtain 4.2 g. of 3',6'-bis(N-methyl-N-phenylamino)-4,5,6,7-tetrachlorofluorane.

70

30

35

40

45

50

55

60

65

70

75

- fluorane as faint greyish-blue crystals melting at 240—241°C.
- A toluene solution of the compound was completely colourless but developed a slightly purplish blue colour immediately on contact with electron acceptor materials such as acid clay, benzenesulphonic acid and hydrochloric acid.
- EXAMPLE 2**
- 10 Example 1 was repeated three times but using 7.3 g. (0.06 mole) of N,N - dimethylaniline, 8.8 g. (0.06 mole) of N - allyl - N - methylaniline or 8.9 g. (0.06 mole) of N - methylacetanilide instead of the 6.4 g. (0.06 mole) of N - methylaniline to obtain in each case the same compound as in Example 1, in nearly the same yield (30—35%).
- EXAMPLE 3**
- 20 Preparation of 3',6' - bis(N - ethyl - N - phenylamino) - 4,5,6,7 - tetrachloro - fluorane.
- A mixture of 10.2 g. (0.02 mole) of 3',6', 4,5,6,7 - hexachloro - fluorane, 7.3 g. (0.06 mole) of N - ethylaniline, 15 g. of zinc chloride and 5 g. of *p* - toluenesulphonic acid was reacted for 2 hours at 180—185°C., for 2 hours at 200—210°C and for 1 hour at 220—230°C. Thereafter, the reaction mixture was treated in the same manner as in Example 1 to obtain 4.8 g of 3',6' - bis(N - ethyl - N - phenylamino) - 4,5,6,7 - tetrachloro - fluorane as faint greyish-blue crystals melting at 225°C.
- This compound developed a slightly purplish blue colour on contact with an electron acceptor material as in Example 1.
- EXAMPLE 4**
- 30 Example 3 was repeated twice but using 8.9 g. (0.06 mole) of N,N - diethylaniline or 7.3 g. (0.06 mole) of N - ethylaniline. In each case, the same compound as in Example 3, i.e., 3',6' - bis(N - ethyl - N - phenylamino) - 4,5,6,7 - tetrachloro - fluorane was obtained in nearly the same yield (35—37%).
- EXAMPLE 5**
- 40 Preparation of 3',6' - bis[N - methyl - N - (*o* - tolyl)amino] - 4,5,6,7 - tetrachloro - fluorane.
- Example 1 was repeated except that 7.3 g. (0.06 mole) of N - methyl - *o* - toluidine was used instead of 6.4 g. (0.06 mole) of N - methyl aniline to obtain 4.5 g. of 3',6' - bis[N - methyl - N - (*o* - tolyl)amino] - 4,5,6, 7 - tetrachloro - fluorane as faint purplish crystals melting at 259—261°C.
- This fluorane compound developed a purple colour on contact with an electron acceptor material as in Example 1.
- EXAMPLE 6**
- 50 Preparation of 3',6' - bis[N - methyl -
- 55 N - (*o* - anisyl)amino] - 4,5,6,7 - tetrachloro - fluorane.
- Example 1 was repeated except that 8.2 g. (0.06 mole) of N - ethyl - *o* - anisidine was used instead of 6.4 g. (0.06 mole) of N - methylaniline to obtain 5.4 g. of 3',6' - bis[N - methyl - N - (*o* - anisyl)amino] - 4,5,6,7 - tetrachloro - fluorane as faint purple crystals melting at 213°C.
- Said fluorane compound developed a purplish-blue colour on contact with an electron acceptor material as in Example 1.
- EXAMPLE 7**
- 60 Preparation of 3',6' - bis[N - ethyl - N - (*p* - anisyl)amino] - 4,5,6,7 - tetrachloro - fluorane.
- Example 1 was repeated except that 9.1 g. (0.06 mole) of N - ethyl - *p* - anisidine was used instead of 6.4 g. (0.06 mole) of N - methylaniline to obtain 5.7 g. of 3',6' - bis[N - ethyl - N - (*p* - anisyl)amino] - 4,5,6,7 - tetrachloro - fluorane as faint greyish-blue crystals melting at 231—232°C.
- This compound developed a blue colour on contact with an electron acceptor material as in Example 1.
- EXAMPLE 8**
- 70 Preparation of 3',6' - bis[N - methyl - N - (*p* - chlorophenyl)amino] - 4,5,6,7 - tetrachloro - fluorane.
- Example 3 was repeated except that 8.5 g. (0.06 mole) of N - methyl - *p* - chloroaniline was used instead of 7.3 g. (0.06 mole) of N - ethylaniline to obtain 4.4 g. of 3',6' - bis[N - methyl - N - (*p* - chlorophenyl)amino] - 4,5,6,7 - tetrachloro - fluorane as colourless crystals melting at 223°C. This compound developed a blue colour on contact with an electron acceptor material as in Example 1.
- EXAMPLE 9**
- 80 Preparation of 3',6' - bis[N - methyl - N - (*m* - chlorophenyl)amino] - 4,5,6,7 - tetrachloro - fluorane.
- Example 3 was repeated except that 8.5 g. (0.06 mole) of N - ethyl - (*m* - chloroaniline) was used instead of 7.3 g. (0.06 mole) of N - ethylaniline to obtain 4.2 g. of 3',6' - bis[N - methyl - N - (*m* - chlorophenyl)amino] - 4,5,6,7 - tetrachloro - fluorane as colourless crystals melting at 160—162°C.
- This compound developed a blue colour on contact with an electron acceptor material as in Example 1.
- EXAMPLE 10**
- 90 Preparation of 3',6' - bis[N - methyl - N - (*p* - chlorophenyl)amino] - 4,5,6,7 - tetrabromo - fluorane.
- A mixture of 13.7 g. (0.02 mole) of 3',6' - dichloro - 4,5,6,7 - tetrabromo - fluorane, 9.3

- g. (0.06 mole) of  $N,N$  - dimethyl  $p$  - chloroaniline, 10 g. of zinc chloride and 5 g. of  $p$  - toluenesulphonic acid was reacted for 2 hours at 185—195°C., for 2 hours at 205—210°C. 60  
 5 and for 1 hour at 220—230°C. to obtain 6.3 g. of 3',6' - bis[N - methyl - N - ( $p$  - chlorophenyl)amino] - 4,5,6,7 - tetrabromo - fluorane as colourless crystals melting at 248—250°C.  
 10 This compound developed a blue colour on contact with an electron acceptor material as in Example 1.

#### EXAMPLE 11

- Preparation of 3',6' - bis[N - methyl - N - ( $p$  - chlorophenyl)amino] - 4,7 - dichloro - fluorane. 15

Example 10 was repeated except that 8.8 g. (0.02 mole) of 3',6',4',7 - tetrachloro - fluorane was used instead of 13.7 g. (0.02 mole) of 3',6' - dichloro - 4,5,6,7 - tetrabromo - fluorane to obtain 3.2 g. of 3',6' - bis[N - methyl - N - ( $p$  - chlorophenyl)amino] - 4,7 - dichloro - fluorane. 20

Example 10 was repeated except that 8.8 g. (0.02 mole) of 3',6',4,7 - tetrachloro - fluorane was used instead of 13.7 g. (0.02 mole) of 3',6' - dichloro - 4,5,6,7 - tetrabromo - fluorane to obtain 3.2 g. of 3',6' - bis[N - methyl - N - ( $p$  - chlorophenyl)amino] - 4,7 - dichloro - fluorane as colourless crystals melting at 200—202°C. 25

This compound developed a slightly purplish blue colour on contact with an electron acceptor material as in Example 1.

#### EXAMPLE 12

- Preparation of 3',6' - bis[N - methyl - N - ( $o$  - tolyl)amino] - 5 - iodo - fluorane. 35

A mixture of 11.7 g. (0.02 mole) of 3',6' - dibromo - 5 - iodo - fluorane, 7.3 g. (0.06 mole) of  $N$  - methyl -  $o$  - toluidine and 10 g. of zinc chloride was reacted for 2 hours at 185—190°C. and for 2 hours at 200—205°C. to obtain 5.8 g. of 3',6' - bis[N - methyl - N - ( $o$  - tolyl)amino] - 5 - iodo - fluorane as faint purple crystals melting at 195—198°C. 40

This compound developed a purple colour on contact with an electron acceptor material as in Example 1.

#### EXAMPLE 13

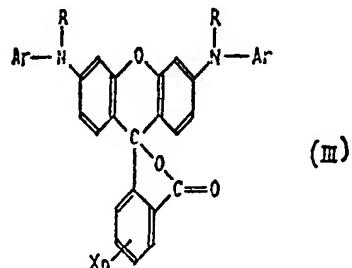
- Preparation of 3',6' - bis[N - methyl - N - ( $\beta$  - naphthyl)amino] - 4,5,6,7 - tetrachloro - fluorane. 50

Example 3 was repeated except that 9.4 g. (0.06 mole) of  $N$  - methyl -  $\beta$  - naphthylamine was used instead of 7.3 g. (0.06 mole) of  $N$  - ethylaniline to obtain 2.4 g. of 3',6' - bis[N - methyl - N - ( $\beta$  - naphthyl)amino] - 4,5,6,7 - tetrachloro - fluorane as colourless crystals melting at 274—276°C. 55

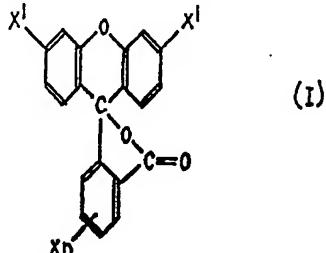
This compound developed a blue colour 60 on contact with an electron acceptor material as in Example 1.

#### WHAT WE CLAIM IS:—

1. A process for preparing a fluorane compound represented by the general formula 65 (III):



wherein X represents a halogen atom, n is an integer from 1 to 4, R represents an alkyl group having from 1 to 5 carbon atoms and Ar represents an aryl group, which comprises condensing a fluorane derivative represented by the general formula (I): 70



wherein X' represents a halogen atom and X and n are as defined above with an aryl-amine derivative represented by the general formula (II): 75



wherein R and Ar are as defined above and R' represents a hydrogen atom or a methyl, ethyl, benzyl, allyl or acetyl group. 80

2. A process as claimed in Claim 1, wherein the condensation is conducted in the presence of zinc chloride and/or  $p$  - toluene-sulphonic acid. 85

3. A process as claimed in Claim 1 or 2, wherein the condensation is conducted at a temperature from 60 to 230°C for from 1 to 6 hours. 90

4. A process as claimed in claim 3, wherein the condensation is conducted at a temperature from 170°C. to 200°C.

5. A process for preparing a fluorane compound as claimed in claim 1, substantially as hereinbefore described with reference to any of the Examples.

GEE & CO.,  
Chartered Patent Agents,  
51/52, Chancery Lane,  
London, W.C.2.  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1972.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

---

— — —

# PATENT SPECIFICATION

(11) 128

5

NO DRAWINGS

- 20 (21) Application No. 47924/70 (22) Filed 8 Oct. 1970
- (31) Conventional Application No. 80540 (32) Filed 8 Oct. 1969 in
- (33) Japan (JA)
- (45) Complete Specification published 23 Aug. 1972
- (51) International Classification C09B 57/00
- (52) Index at acceptance C4P D1S



## (54) PROCESS FOR PREPARING FLUORANE COMPOUNDS

(71) We, FUJI PHOTO FILM CO., LTD.,  
a Japanese Company, of No. 210, Nakanuma,  
Minami Ashigara-Machi, Ashigara-Kamigun,  
Kanagawa, Japan, do hereby declare the  
5 invention for which we pray that a patent  
may be granted to us, and the method by



wherein R and Ar are as defined above;  
R' represents a hydrogen atom or a

## ERRATA

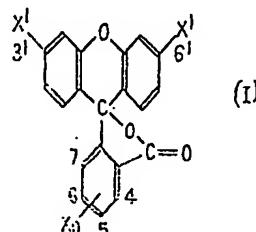
SPECIFICATION No. 1,286,885

Page 4, line 6 for 3',6 read 3',6'

Page 4, lines 17 to 23, Delete whole lines

THE PATENT OFFICE  
16th October 1972

20 wherein X represents a halogen atom; n is  
an integer from 1 to 4, R represents an alkyl  
group having from 1 to 5 carbon atoms and  
Ar represents an aryl group, which comprises  
condensing a fluorane derivative represented  
by the general formula (I):



25 wherein X' represents a halogen atom and X  
and n are as defined above with an arylamine  
derivative represented by the general formula  
(II):

colour-forming ability is not affected by  
exposure. Also, the dye formed on contact  
with an electron-acceptor material is  
fast to light. The fluorane compounds  
presented by the general formula (III),  
however, are very effective as precursors or  
formers for pressure-sensitive, heat-  
and photo-sensitive copying papers (the  
developed by contact with an  
electron-acceptor material under pressure, is  
light).

Several compounds similar to those  
presented by the general formula (III) are  
(see Beilstein, Handbuch Der Org  
Chemie, Vol. 19, 349). Examples of  
known compounds are represented by  
following formulae Ia and IIa but the  
compounds cannot be obtained as co  
crystals. It is believed that they exist  
in the forms represented by the general  
formulae Ib and IIb, which are dye

SEE ERRATA - SLIP - ATTAC